GUIDANCE DOCUMENT
FOR THE
ELEMENTAL CHARACTERIZATION
OF
LIQUID WASTE SAMPLES

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Environment Ontario

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Minister

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INTRODUCTION

A key component of the Municipal/Industrial Strategy for Abatement (MISA) program is the development of a comprehensive database of contaminant discharges to surface waters in Ontario. During the initial phase, direct discharges from major industrial and municipal sources are to be sampled and analyzed for the concentrations of a number of substances in order to characterize these effluent streams. MISA regulations (1) require periodic sampling and analysis at prescribed intervals for an on-going assessment of rates of discharge, effects of abatement measures, etc., supported by random monitoring by the Ministry of the Environment (MOE). Additional information describing the analytical parameters of interest can be found in the MISA Effluent Monitoring Priority Pollutants List (EMPPL) (2).

This document presents an overview of the analytical approach adopted by MOE Laboratory Services Branch to meet the analytical needs for monitoring the majority of the elemental parameters. For a few parameters, additional special techniques are required but these are not described in detail. Since this document is a guideline, not a formal analytical method, the description simply highlights the features of the approach. It should not be used as a procedure for analysis of MISA samples. If more detailed information is required then requests for the current method write ups should be made to the Quality Assurance Office of the Laboratory Services Branch (3).

1. Analytical Approach

Analytical methodologies in inorganic chemistry are traditionally described as qualitative, semi-quantitative, or quantitative. Qualitative methods are employed to detect the presence or absence of analytes in a sample. Quantitative methods are the most precise and accurate. An overall accuracy of up to 10%-15% may be acceptable for any given determination, although better accuracy is certainly desirable and frequently achieved. Semi-quantitative methods fall between these two approaches. Higher overall uncertainties in the final results may be tolerable, compared to a result from a quantitative method, but the final product is still a numerical result with an assignable uncertainty. More typically, especially with semi-quantitative multi-element methods, accuracies for most analytes are comparable to those achieved with a quantitative method, and the higher uncertainties are attached to only a few analytes.

The large number of potential contaminants and the diversity of sources to be monitored, each with its own mixture of waste materials, precluded the development of a single, universally applicable quantitative analytical method at this time.

To deal with these difficulties, the Ministry of the Environment has developed a set of methods using various techniques, including plasma spectroscopy, atomic absorption spectroscopy, colourimetry, and fluorimetry. Plasma spectroscopic techniques are used for almost 90% of the elements required to be characterized by MISA because they are sensitive, multi-element, and relatively specific. They are employed in most major laboratories, have had wide application to a variety of sample types, and form the core of the MOE methods for elemental characterization.

A sample preparation step is necessary before introducing the sample into the analytical instruments. Strictly speaking, the method is applicable only to single-phase liquid waste samples; that is, the samples either do not contain any solid material, or else the solid material present in the samples can be decomposed by suitable digestion procedures.

When applied for purposes of open characterization the methods are designated as semi-quantitative. This is because of the uncertainty regarding the nature of the samples which might be encountered. This uncertainty arises from two sources: variable sample matrix, and inter-element interferences.

In quantitative methods, the analysis is limited to samples whose major composition does not change significantly. Standards and technique can thus be matched to this particular sample matrix. This is not practicable for monitoring industrial effluent streams, given the variety of municipal and industrial sources of pollutants in the province; hence, the sample matrix is not standardized. Inter-element interferences are encountered (in common with most multi-element techniques) which add an additional uncertainty to the final result. A significant error may be introduced if an interfering element is not detected. The reliability of the method is increased with inclusion of additional scanning capabilities; interfering elements can be determined and corrections applied, and it is possible to detect previously unsuspected contaminants.

2. Elements of Interest

In addition to hydrogen and oxygen, water has 10 principal constituents (4,5,6): Ca Mg Na K C N Si P S Cl.

Another 28 elements are typically detected in water at low concentrations: Li Be B F Al V Cr Mn Fe Co Ni Cu Zn As Se Br Rb Sr Mo Ag Cd I Cs Ba Hg Pb Ra U.

Thirteen elements normally occur at extremely low concentrations, except when concentrations are elevated by pollution: Ti Ga Ge Zr Pd In Sn Sb Te Ta W Tl Bi.

The Ministry methods can determine the concentrations of 70 elements: Al Sb As Ba Be Bi B Cd Ca Ce Cs Cr Co Cu Dy Er Du Gd Ga

Ge Au Hf Ho In Ir Fe La Pb Li Lu Mg Mn Hg Mo Nd Ni Nb Os Pd P Pt K Pr Re Rh Rb Ru Sm Sc Se Si Ag Na Sr S Ta Te Tb Tl Th Tm Sn Ti W U V Yb Y Zn Zr.

3. Alternative Techniques

A variety of analytical techniques are available for the measurement of elemental concentrations. They can be broadly categorized as either single-element or multi-element techniques. Common techniques are:

flame atomic absorption spectroscopy (AAS)	single
graphite furnace AAS (GFAAS)	single
polarography	single
colourimetry	single
ion chromatography	single/multi
ICP optical emission spectroscopy	multi
DCP optical emission spectroscopy	multi
ICP mass spectroscopy	multi
instrumental neutron activation analysis (INAA)	multi
energy-dispersive X-ray (XRD)	multi
proton-induced X-ray emission (PIXE)	multi

Additional techniques, such as electron microscopy with ion microprobe, are capable of excellent sensitivities but are more appropriate for analysis of surfaces or of individual particles, etc., rather than determination of the total elemental content of bulk samples.

No single technique can be recommended. Many practical concerns should be considered when selecting one (or more) techniques for use with industrial wastes. Sample throughput for the single-element techniques has been increased through technological advances such as microcomputer controllers, and flow injection techniques are available which can employ complexing agents and spectral detectors for the determination of many metals. But the sequential nature of these techniques, requiring separate set-ups for each analyte, remains.

Multi-element techniques are preferred because of the number of parameters to be measured, provided the techniques have the necessary sensitivity and specificity. There are both common and unique limitations of all multi-element techniques. For instance, energy-dispersive X-ray analysis may not achieve the same sensitivities as plasma spectroscopy, but its solid-sample capability may be much more appropriate (and avoid or minimize the sample digestion step) when analyzing solid industrial wastes. A comprehensive laboratory program would include a suite of methods based on several techniques which would cover the range of sample types and concentrations expected.

Practical concerns such as instrument availability, capital and operating costs, laboratory space, the availability of trained personnel, etc., are also important factors in selecting a technique for developing a routine method. The following discussion applies particularly to plasma source optical emission spectroscopy but the general approach would be similar with any other technique. The discussion presents an overview of plasma-source optical emission spectroscopy, particularly those characteristics which are relevant to the analysis of MISA samples.

BASIC PRINCIPLES OF PLASMA-SOURCE EMISSION SPECTROSCOPY

1. Development Plan

Development of a spectroscopic analytical method includes many steps:

- selection of elements
- estimation of the concentration range expected for each analyte
- selection of analytical wavelengths
- optimization of instrument parameters
- determination of detection limits (sufficiently sensitive?)
- verification of response curves (linear? is a buffer necessary?)
- preparation/acquisition of standard solutions
- optimization of method parameters (integration time? multiple exposures?)
- examination of inter-element effects (spectral overlap or coincidence)
- determination of precision (short term; long term)
- establishment of Quality Assurance/Quality Control protocols
- method validation (analysis of standard reference materials, duplicate samples, spiked samples; interlaboratory comparisons)
- data handling and reporting procedures
- method write-up

Development of a suitable sample preparation procedure may take place concurrently.

The development is rarely a step-by-step process. For instance, in spectroscopy it is desirable to use the most intense emission line for each element, as might be found in line libraries (7), so that the highest sensitivity can be achieved. However, later examination of inter-element effects may show significant interferences on some elements; a less sensitive interference-free wavelength may be substituted. Alternatively, a numerical correction factor may be calculated to remove the inter-element interference.

2. Sample Preparation

Liquid industrial wastes discharged into surface waters typically contain solid-phase material in addition to the predominant liquid phase. A digestion is useful before analyzing such samples for the total element content. Experience at the MOE laboratory has led to a two-group sample classification:

type 1 - clear, coloured, some sediment
type 2 - oily, sludge, hard to digest

Type 1 samples are digested with a combined thermal/acid treatment. The treatment is carried out in two steps, the first with concentrated nitric acid, and the second with aqua regia. Type 2 samples are ignited in a muffle furnace before carrying out a thermal/aqua regia digestion. Both types of samples are readied for introduction into the analytical instrument by diluting to a fixed volume with double distilled water.

3. Plasma Excitation Sources

Emission spectroscopic techniques use high energy sources to excite the analyte atoms in the sample. Subsequent relaxation of the atoms is accompanied by the emission of photons of light with a characteristic wavelength (equivalent to a characteristic energy). Each element has a number of these emission lines, the exact wavelengths depending on the atomic structure of the element. The intensity of a line, that is, the number of photons with the same wavelength, is proportional to the number of atoms excited and, hence, is directly related to the concentration of the element in the sample. Details can be found in standard texts (8). The emission spectra from a sample containing significant amounts of several elements can be quite complex, requiring care in the selection of the analytical line to minimize overlapping of lines from different elements.

Thermal flames are sufficiently energetic to excite some elements, particularly at high concentrations, but plasma sources are preferred for multi-element techniques because of the more intense discharge. Two types of plasma sources are commercially available at present: direct current (DCP), and inductively-coupled RF plasma discharges (ICP). The aqueous sample extract is most commonly introduced into the plasma discharge through a nebulizer, which produces a fine aerosol mist that is carried into the plasma by an inert gas stream. The ICP discharge can be extinguished if a large amount of material is suddenly introduced into the sample stream. The DCP is somewhat more robust in that it can tolerate higher sample loadings, but long-term precision may be degraded by wear of the electrodes.

4. Spectrometers

The light from the plasma discharge is directed into an optical spectrometer, which can discriminate between photons of different wavelength. Spectrometers fall into two general classifications, sequential and simultaneous (also referred to as monochromators and polychromators). Either type of spectrometer can be used. Simultaneous spectrometers have a separate detector and electronics card for each wavelength to be detected. The light is diffracted by a an optical grating such that photons with different wavelengths are distributed along an arc. The detectors are located along the arc at specific positions; the physical size of the spectrometer can thus be a limiting factor. Initial set-up may require more time than with a monochromator, and it is more difficult to select alternate or additional lines. A sequential spectrometer has a single detector which is used for all wavelengths within a spectral region. Different wavelengths are selected by rotating a grating between the plasma and the detector. The position is controlled by a computer, which makes scanning of different wavelengths or wavelength regions very easy.

Both types of spectrometers have advantages and disadvantages. Analysis time with sequential spectrometers is proportional to the number of analytical wavelengths and can become excessive with a large number of analytes; simultaneous spectrometers measure all of the analytical lines at the same time and can maintain a high sample throughput. On the other hand, additional lines cannot be added to a simultaneous spectrometer without opening the spectrometer and physically adding or moving a detector. Recent developments in instrumentation have blurred the distinction between simultaneous and sequential spectrometers, and combination or enhanced instruments are now commercially available.

The importance of instrument flexibility cannot be overstated when dealing with complex and variable sample matrices such as industrial effluents. Anomalous results can be checked by repeating the analysis using another analytical line, or by scanning through a wavelength region and visually examining the results for unusual peaks or background shifts.

High resolution spectrometers are required for accurate work. Resolution refers to the capability to discriminate between closely spaced lines. Higher resolution is normally required for complex sample matrices such as industrial wastes, which have a large number of analytical lines, than is required for simpler sample matrices such as drinking water. While concentrations are lower in the latter type of sample, requiring a higher sensitivity, the optical spectrum is simpler and likely to have fewer overlapping lines than the spectra from industrial waste samples.

An additional consideration is whether the spectrometer should contain air, be purged with inert gas, or be evacuated. Because oxygen strongly absorbs light at wavelengths less than 200 nanometers, purged or evacuated systems are necessary for the

measurement of analytes such as sulphur at these low wavelengths.

5. Biases and Interferences

Biases and interferences arise from a number of sources. Samples must be collected according to established protocol, in approved containers, and with any necessary preservatives added in the correct amounts; otherwise, results from the analytical laboratory will be invalid. Chemical biases can be introduced by contamination or by a digestion procedure which recovers less than 100% of each analyte of interest. Both of these biases may exist in the preparation of industrial waste samples for spectroscopic analysis, and can limit the overall accuracy of the method. For instance, the analytical instrument may have good sensitivity for Ag, but a method which uses aqua regia to digest samples would be inappropriate because of the insolubility of AgCl. Biases arising during routine analysis of samples can be controlled to within tolerable levels by incorporating a system of instrument blanks, reagent blanks, composite standards of known composition, analysis of duplicate samples, etc. The MISA regulations (1) include a specific QC run protocol for analysis of liquid waste samples by private laboratories.

A spectral bias can occur when the baseline intensity in the region of an analytical line differs between standard and sample. This is the normal circumstance because the background intensity is a function of the number and concentrations of all constituents in the sample. The bias can be removed by applying a background correction: the concentration of an analyte is determined not from the intensity at the analytical wavelength alone, but from the net intensity calculated as the difference in intensities between the analytical wavelength and a wavelength offset from the analytical line. The offset must be selected so that it is in a region that does not include any significant emission lines. Either a 1-point correction or a 2-point correction can be applied; 2-point corrections are necessary when the background intensities on either side of the analytical line do not change by the same amount. Background corrections are recommended when a) it is known that the background intensities of samples are different from those of the standards; b) it is certain that no spectral feature of an interfering species could be located at the selected wavelength for background correction; c) the concentration of the analyte will never be sufficiently high so that broadening of the analytical line will cause negative determinate error during the process of background correction.

Spectral interferences are caused by overlapping of lines from different elements. Note that when a wavelength region is scanned and examined visually, the intensities from the analytical wavelengths do not appear as discrete lines, but rather as peaks with a finite width. Closely spaced peaks may overlap to give a composite peak, or if sufficiently close, may appear as one single peak. The ability to separate peaks depends on the resolution of

the spectrometer. If an analytical line cannot be fully resolved from a neighbouring interfering line, then an inter-element interference is present. A correction factor can be determined by analyzing standards with a known concentration of the interfering element, and recording the apparent concentration at the analyte line of interest. The concentration of the interfering element can then be determined in samples (using an alternate wavelength), and the amount of the interference can be calculated and subtracted from the original analyte line.

Such interferences have a significant effect of the accuracy of the final result. There is a larger error associated with a corrected concentration than with a result obtained in the absence of inter-element interferences. This is because the corrected result requires three empirical measurements: the concentration of the target analyte, the concentration of the interfering analyte, and the inter-element correction factor. There are uncertainties associated with each of these, which increase the uncertainty in the final corrected result. Standard texts (9) can be consulted for a description of how errors propagate with each additional mathematical operation. Possible inter-element interferences should be examined for each analytical wavelength; a list of potential interferences can be compiled by examining line libraries for strong lines in the region of the desired analyte wavelengths. The presence of any inter-element interferences can then be verified experimentally.

A considerable error may be introduced by matrix effects. These occur when the nature o the plasma discharge is changed by the presence (or absence) of one or more elements. Matrix effects are reduced to negligible levels when the major constituents of the samples have concentrations similar to the concentrations in the method standards. When the major constituents have different concentrations or are in different proportions, then the instrument response to a given concentration of an analyte is no longer identical for both samples and standards. Matrix effects are commonly encountered in solutions with high concentrations of salts or easily ionized species.

Different sample matrices should be expected when establishing a method for the analysis of effluent streams from many different sources. With a limited number of source types, the sample matrix may be sufficiently consistent that the method standards can be matched to it. For characterization of a variety of industrial source types, results should be closely screened before approval.

6. Method Validation

The preferred means of establishing the validity of an analytical method is to analyze a number of standard reference materials (National Bureau of Standards, Environmental Protection Agency, National Research Council of Canada, etc.) which are similar to the sample types expected, and which have certified

concentrations of elements. Synthetic standards prepared in the laboratory may also be employed but only after their composition has been determined accurately by established methods. It should be possible to trace any result back to a certified primary standard.

If there is no standard reference material matching the expected sample matrix, additional validation steps are needed. The simplest approach is to do a paired comparison with results from one or more established techniques. It is important to use a statistically significant number of samples in such a comparison, and to include both typical samples and samples which cover the entire concentration range of interest.

Method Detection Limits must be determined to see whether the final method has sufficient sensitivity to meet the requirements of the MISA. Standardized procedures (10) have been developed to derive these figures for each analyte.

Additional comparisons can be made using spiked samples. To verify the complete method, aliquots of elemental standards of known concentration can be added before digesting samples. Samples can also be spiked after digestion, but the results would normally be indicative of instrument performance only.

Anomalous results encountered during analysis can also be verified using spiking and/or dilution. If the analyst suspects an uncorrected interference, the sample can be re-analyzed after spiking separately with the suspected interfering element; a result which is statistically different from the first result indicates an inter-element interference. Alternatively, if a matrix effect is suspected, the sample could be diluted and re-analyzed; after correcting for the dilution factor, there should be no statistical difference.

Matrix interference is a non-trivial problem when analyzing liquid industrial wastes by atomic spectroscopic techniques. In extreme cases, where the sample matrix is significantly different from the method standards, it has been found that concentrations of analytes may even be higher in the diluted sample, than in the original sample. It is imperative that all results be screened by an experienced specialist for potential problems such as these.

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